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On the subsidence of particles in liquids.

Case

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ON THE SUBSIDENCE OF PARTICLES IN LIQUIDS.

BY

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While connected with the State Geological Survey of California, 1860–'64, my attention was turned to the relations of saline and alkaline waters to the precipitation of suspended matter. There were abundant means of observation in the field, but no laboratory experiments were made. Soon after the republication by the Ray Society, in 1866, of Robert Brown's observations on the movements of minute solid particles in liquids, I began a series of experiments on these "Brownian movements" in their relations to sedimentation, but unfortunately I have now no systematic record of the experiments made previous to February, 1875, since which time the experiments have been much extended and systematic records have been kept of many of them. In 1877 I published some of the observations in their relations to agriculture (*11th Ann. Rep. Com. State Board of Agr., p.* 73–83), and in 1880 further observations in their sanitary relations—on the action of muddy water on sewage—*Public Health Papers and Reports, vi*, 334), and in 1881, in a lecture (not published further than in ordinary newspaper reports), I further discussed the matter in connection with the problem of the jetties at the mouth of the Mississippi River.

Since 1877 the experiments have been much expanded and have gone on along several lines of investigation. They extend to a considerable number of clays, soils and other suspended matter, and the records and notes have now become somewhat voluminous. Inasmuch as prolonged time is an element in some of the experiments, and as this meeting enables me to exhibit some of the specimens to the academy, I take the occasion to report on some of the observations made and inferences deduced from these long-continued observations and still unfinished experiments.

It is a matter of common observation that fine clays and muds may remain long suspended in fresh water, but it is commonly believed that if the water be left at rest complete sedimentation takes place within a few weeks or months at most, leaving the water clear; that salts of many kinds hasten the settling, and that also acids hasten it. Some writers have stated that dilute alkalies retard it and may prolong it even indefinitely, and numerous observers have noticed that during the subsidence of clays in perfectly still fresh water they are often disposed in layers or strata of different degrees of density, giving to the liquid different degrees of opacity.

In this paper I do not purpose to review the history of our knowledge of this subject, nor to discuss the published observations or experiments of others; that is left for a future paper. It will better serve my present purpose to discuss my own experiments (with the exhibition of a few of my specimens), with only so much allusion to the labors of others who have wrought in the same field as is necessary for an understanding of my own work.

If clays containing some fine sand, as most clays do, are thoroughly mixed with pure fresh water and then allowed to stand in perfect quiet in a suitable vessel, a portion, including all the coarser particles, soon falls to the bottom, but a considerable portion remains longer suspended. The water may become nearly clear in a day or two, or finer material sufficient to render the liquid opaque in vessels three or more inches in diameter may remain suspended for weeks.

In these latter cases the liquid usually becomes disposed in strata; that is, the suspended matter will not fade gradually in density from the bottom upwards through regularly diminishing

opacity to the top, but will rather be disposed in successive layers, the limits of each more or less well defined.

Different specimens of clays and soils behave quite unlike in this respect, so far as the details go. A few do not show these strata at all, the suspended matter fading gradually and regularly in density, and such clays usually settle comparatively rapidly. Others show the character but feebly; there may be but two such layers, or, if more, the limits of each may be very illy defined. Some show as many as six or eight, or even more, in which cases they are of unequal thickness, and sometimes the limits of each are surprisingly distinct.

If left perfectly quiet, the heavier go down first, and at last all are down but one, and the liquid is then uniformly opalescent from bottom to top. This may be after a week or two or it may be only after many months. With further quiet this opalescense gradually fades evenly from top to bottom, the rapidity of this clearing of the liquid being modified by several external conditions.

The fading of this opalescense by subsidence goes on slower in the light than in the dark, but how nearly this is related to changes of temperature I have not been able to determine, as any place at my command from which light is excluded is subject to less fluctuation of temperature than where it is abundant. The nearest approach to similar conditions other than light has been in an instrument closet in my lecture-room, built against a firm interior brick wall, the upper part of the case being closed by glass and the lower part by wooden doors. When similar specimens have been exposed in these two cases at the same time, the fading of the opalescense by subsidence has been more rapid in the dark case than in the adjacent light one.

If the experiment goes on in a place of perfect quiet and in the dark, and where the daily changes of temperature are slight and very gradual, then the opalescense gradually fades with time; but how long before it will entirely fade away and the liquid become clear by the subsidence of the particles (if indeed it ever will) I cannot say, but certainly not in six years, some of my samples having now stood longer than that time.

If, however, the experiment is conducted in an ordinary lighted room, with the fluctuations of temperature incident to habitation or use, then after a time the opalescense ceases to fade; it may remain stationary as to intensity, or it may increase and diminish with the seasons and other fluctuating conditions. How much such fluctuation in opalescense is owing to convection currents produced by the fluctuations of temperature, and how much to other causes, I have found no means to determine.

The color of this ultimate uniform opalescense is usually milky, but with some ferruginous clays it is red, brown, or of different shades of amber; with certain other clays it has various shades of pale green and yellowish green. This is strikingly the case with certain clays from the bad lands of Wyoming, the shades of color of which remind one of the tints of some of the Swiss lakes as seen from the alpine heights above them, which tints and colors I suspect may be due to a similar cause.

Temperatures above that found naturally in the free air and also below the freezing point are each accompanied with their special phenomena.

The boiling of clays in a great excess of water tends to reduce them to the finest division, and this is the method employed by Professor Hilgard in his elaborate and most instructive investigations on the physical conditions and composition of soils. Some clays go to pieces easily on boiling, while others, according to this authority, have to be boiled for many hours, it may be for days (and with precautions to prevent flocculation), before the process is complete. I find

that many, if not most, clays behave very differently in hot water from what they do in cold, and different clays differ in behavior in hot water.

Some clays which go to pieces easily in cold water, and which settle slowly if the water remains cold, settle rapidly if the water be raised to near the boiling-point. Some such clays which have been experimented upon, which will remain suspended in large quantity for many days if kept cold or at ordinary temperatures, if the water be gradually heated, when a certain temperature is reached the clay suddenly flocculates or curdles, and settles in a very bulky, mobile mass long before the water begins to boil, and during the boiling there is this constant tendency to flocculate, the suspended matter behaving much as it does in the presence of certain chemicals, to be noted later. If the heat be removed and the liquid allowed to cool slowly, the phenomena are reversed. While hot, much of the suspended matter curdles and falls in a very bulky, mobile mass, which if shaken soon falls back again until the water reaches a certain reduction of temperature, when, if the material be shaken, it will require several days for any part to become so nearly clear as the upper part would be in a few minutes if hot. I think it probable that some of the colors described in the hot springs of the Yellowstone region may be related to the behavior of clays in hot water.

Again, freezing affects the suspension. If water holding suspended particles be frozen solid and then be thawed again, it is rendered much clearer by the operation. The mud becomes largely disposed along certain lines of crystallization in the ice, and if this be slowly thawed in the quiet, it falls and does not rise again. In one set of my experiments the water in which a red ferruginous clay was suspended froze partially solid, a portion of the liquid being entirely surrounded by ice. In the liquid the suspended matter was ultramicroscopic, but in the ice the red material was concentrated in visible particles along certain lines, curiously disposed relative to the crystallization and to the inclosed air-bubbles. Stereoscopic photographs show the arrangement in the mass, but drawings are very unsatisfactory.

In one such case, when the liquid, much cleared by the freezing, was placed near a window where the sun struck it a little while each day, it soon became turbid again, possibly by convection currents caused by the sun's heat; but similar specimens melted in the dark and kept in the dark remained as clear as the freezing had made them. Changes in ink by freezing are familiar to all, and probably due to the same cause.

Some clays, if thoroughly dried, and then moistened again, and then frozen and thawed in a wet state, behave very differently in water before and after such freezing.

The fallen sediment from different clays varies greatly in hardness and tenacity, the differences not following the relative proportions of sand in the original material under experiment. With some samples, even of very fine clay, the suspended portion may be very large and the dense turbidity remain a long time, and yet the sediment which does fall be very firm in a day or two, while others may fall speedily into a bulky mass as mobile as the water itself, which shrinks and is compacted very slowly indeed in the water. Some sediments, when they have stood a few days or weeks in the liquid from which they have subsided, are so firm that it requires much and long agitation to again diffuse them through the water; others, after several years' standing, may be entirely diffused by a few seconds' agitation.

It is obvious that each and all of these various facts have their geological significance, and phenomena immediately suggest themselves where they certainly or possibly play a part.

Thus far I have only described the behavior of clays and suspended matter to fresh water, and in many of my experiments distilled water has been used.

In solutions of various kinds, the phenomena are very different, and experiments have been conducted with various acids, alkalies, salts, extracts, and neutral organic substances.

Some of the more general facts are well known and widely applied. The use of certain salts to clear turbid waters, and of organic substances to correct unwholesome waters, are of wide application, and have been known from antiquity. (See *Exodus*, xv, 23.) Alum is used in many countries where the drinking water is turbid. I have often heard of its use in the Mississippi Basin; also in South America and Europe; and Mr. Arnold Hague tells me that he found it in universal use in the Loess country of Northern China, where it has been used for this purpose for ages.

The rapidity of sedimentation in the presence of certain salts and acids, as contrasted with the behavior of the same material in fresh water, is indeed striking. I exhibit one specimen to the academy especially notable in this character, and which has been used to illustrate the general fact to my classes. The original is a very hard, greenish, eocene clay, from the Niobrara region, which when ground up in pure water settles very slowly. For class-room illustration a quantity which has stood some days, for the coarser parts to settle, is decanted and divided into two equal portions at the beginning of the lecture. To one a solution of common salt is added, to the other an equal volume of distilled water, that the opacity of the two be equal at the start. Before the close of the lecture the upper part of the one will be clear, or nearly so, the other apparently unchanged. The specimen I exhibit to the academy was thus used; it is the portion in pure water, and after over thirty months of standing at rest is not yet so clear as its companion portion in salt water became (during the lecture) in less than thirty minutes.

When a solution of common salt (or of sea-water) is added to muddy water, the suspended clay curdles or flocculates and immediately begins to fall, and in a comparatively short time the liquid becomes clear. If the clear part be decanted, an equal volume of distilled water be added, the sediment again diffused through the liquid by agitation, and the process be repeated, the saltness of the solution being reduced at each dilution, the behavior of the same identical clay in the same quantities of solution of different degrees of strength may be observed, if time enough be given to the observations. We may say, in a general way, that the stronger the solution the quicker the precipitation; but the rapidity is not directly as the quantity of salt dissolved. Reducing the saltness one-half does not necessarily double the time required for the solids to settle. With some clays the precipitation in a solution as strong as sea-water, or even half as strong, is as much in thirty minutes as in as many days, or even months, if the water be pure; and if the amount of salt be increased, the rapidity of sedimentation is not correspondingly increased. On dilution by decantation as described, the precipitation becomes slower and slower. When the liquid contains but one-tenth or one-twentieth the amount of salt found in sea-water, the precipitation becomes very slow, but in a few weeks or months the liquid becomes as clear and pellucid as the clearest natural waters. As the dilution goes on and the water contains less and less salt, its capacity becomes greater for holding the clay in suspension, both as to the quantity that may be suspended and the length of time it will hold it. The identical mud previously thrown down rapidly in salt or brackish water, when the water becomes fresh is again picked up, on agitation, and is again held in suspension. This may be repeated indefinitely. Each time salt is added the settling is hastened, and with each freshening the mud is again suspended longer.

I have tested this with numerous muddy waters produced artificially, and also on the actual river water taken from the Mississippi River below New Orleans, and from the Missouri River, 2,800 miles above, and on other natural muddy waters. Different specimens behave somewhat differently as to degree and in details, but the essential facts are the same for all the samples I

have experimented upon. I believe that the phenomena have an importance not heretofore given to them either by geologists, physical geographers, or engineers.

The formation of bars at the mouths and in the channels of rivers, and the distribution of silt on the floor of the ocean and of lakes, have usually been discussed and considered from the hydraulic side only, the direction and velocity of the current have been considered as the only factors of any considerable importance, but I believe that the chemical composition of the water plays an essential and controlling part in the effects produced.

The phenomena attending the formation of bars at the mouths of rivers which empty into fresh-water lakes, and the depositions which take place in the channels of rivers where the water remains fresh all the year through, are very unlike those attending the formation of bars in salt water at the mouths of muddy rivers, or the silting of the channel just within the mouths of such rivers, where the water becomes brackish before reaching the sea.

In fresh-water rivers and at their mouths in fresh-water lakes, the more obvious changes in the bars take place only at the time of floods, and the movement and deposition of the material are in strict accordance with hydraulic laws. The "hydraulic value" of particles of known size and specific gravity has been experimentally determined with great care and accuracy. The deposition of the finer material takes place in the still waters, and at low water and is comparatively slight in quantity in any one year.

But when a muddy river enters salt water, chemical laws interfere with the purely mechanical ones, another set of phenomena are introduced, and the growth of the bar is different. Then the rate of deposition is affected by the salt more than by the current, and velocities which would be much more than sufficient to carry the finer suspended matter indefinitely if the water were fresh, entirely fail where the water is brackish or salt. Practically it is the degree of saltness which controls the deposition.

In the phenomena exhibited at the mouth of the Mississippi River we see these principles manifested on a stupendous scale.

At time of flood, when the whole water is fresh to the bottom of the river and to its very mouth, then no considerable deposition occurs in the channel within the mouth; the mud is carried outside and largely deposited on the outer slope of the bar, notwithstanding the agitation by the waves at that point. At the same time the channel within the mouth is scoured out and the inside of the bar is more or less abraded, or, as various engineers have expressed it, the bar is "pushed out into the Gulf" by each high water.

At low water the salt water from the Gulf runs back into the river, first as a stratum on the bottom, with a layer of the lighter fresh and muddy water over it; then later the river becomes brackish to its surface, this condition extending to the head of the passes, or further, according to the season and the amount of water. Then a large deposition always takes place on the inner slope of the bar, and in the channel within the mouth, and up to the head of the passes. I was told on the spot that this takes place every year, and that since the jetties have been built, the required depth for navigation is only then maintained between the jetties by some dredging. As the channel is closely watched and soundings made every week from the head of the passes to the Gulf, the phenomena are easily studied. And let it be borne in mind that the time when this deposit takes place within the mouth is when the proportion of mud to water is at the least, and is very much less than at high water.

When the floods of the next year come, and the waters again freshen to the bottom of the river, this deposit is picked up again by this fresh water and is carried out to the salt water, as already described. It is precisely analogous to the picking up of the material in the experimental

flasks by successive freshenings. This picking up from within the river and the inner slope of the bar is by water already much heavier loaded with clay than was that from which the low-water deposition took place. Abrasion within the channel often takes place rapidly where some change of current occurs, and deep places are locally excavated to such depths that the jetties have to be protected from undermining by temporary or permanent wing-dams. The high water of the year of my visit had excavated one place to the depth of 120 feet where the water had been very shoal before the building of the jetties. A short wing-dam at the time of my visit was directing the low-water deposit into this hole, and its depth had already been reduced 40 feet.

Some of the specimens exhibited to the Academy are of mud dredged from the inner slope of the bar just within the jetties, when the turbid fresh water formed a layer 14 feet deep over the clearer salt water then on the bottom of the river channel. The material is a very unctious, tenacious clay, which becomes very tough on drying. It is as smooth as soap in the hands, but gritty with very fine sand between the teeth. The microscope shows the sand to be very minute and the finer grains very active with "Brownian movements." When agitated in fresh water a large quantity of this mud is suspended, and the liquid remains opaquely muddy for a comparatively long time, but it flocculates and settles quickly when mixed with sea-water. I have made many experiments with the several muds obtained at and near the jetties, and with river water obtained above the passes, where the water was entirely fresh, and all show essentially the same phenomena when in waters of the same freshness.

My belief is that the deposition in the channel within the mouth at low water is directly and chiefly due to chemical causes; that the scouring out at time of high water is also due to chemical causes, the velocity of the current being secondary; that a given volume of salt water, having a given velocity, will not suspend and transport an amount of clay which the same volume of fresh water, having the same velocity, would suspend and transport indefiintely; that fresh water with a given velocity will pick up from the bottom and scour out deposits which salt water of the same velocity will not, notwithstanding its greater specific gravity.

This is not only in accordance with my experiments, but it seems to me to be abundantly illustrated in the delta phenomena of the Mississippi. The local abrasions between the jetties at floods show what has occurred at successive steps all the way to the head of the delta. When the Gulf extended much farther inland, then the water was shallow both inside and outside the mouth, as it is now, but as the delta grew and the bar was "pushed out into the Gulf" by successive floods, the deep river channel followed it up from behind, the mud being picked up and carried out as the water freshened, just as it now is done between the jetties. From above New Orleans to near the head of the passes, so far as the water continues fresh at all times of the year, the channel is deep, usually more than 70 and often 100 or 120 feet deep; but all this distance the water must have been shallow when the mouth of the river was at the successive points. The shoaling of the river from where the water becomes salt, the upward slope from the head of the passes to the crest of the bar, up which slope the river must run at flood and down which the heavier salt water runs when not crowded out by floods, the deposition on the outer slope of the bar at high water and on the inner slope at low water, the deposit within the mouths when enough salt water gains admission there, and the scouring out of this again as the river freshens are all in strict accordance with this theory. My experiments explain phenomena the causes of which have heretofore been so much in dispute between the engineers who have discussed the improvement of the mouth for navigation.

Some of these phenomena were observed in connection with this very question so long ago as 1838 by W. H. Sidell, who experimented upon the action of acids, various salts, sea-water, &c.,

and concluded "that the earthy matter is deposited more suddenly than would be the case if it depended on the check of velocity alone" (*Report on the Hydraulics and Physics of the Mississippi*, Appendix, p. 500). It is very remarkable that these experiments and observations attracted no more attention during the later discussions of the problem.

The same principles explain the distribution on the floor of the ocean of the finer materials brought from the land. Notwithstanding the depth and extent of the oceanic currents, all the solids materials brought to the sea are deposited near the land. All the recent observations show that but little is carried far from shore; the profound depths of mid-ocean contain but little or none of it, and we are all familiar with the clearness and intense blue of the waters there.

My experiments have extended to a considerable variety of salts, but more especially to the chlorides, sulphates, and nitrates, to mixtures of these, and to organic substances, both colloids and crystalloids, to carbhydrates and albuminoids, extracts of woods, herbs, and of peat, and in a large number of these, clearing was more rapid than in pure water. The effect of certain neutral colloid organic substances, like the gums, is to favor suspension, as is well known.

The action of some of the salts is obviously aided in certain cases by the formation of permanent chemical compounds. This is notably the case in the reaction of alum in certain solutions containing chlorid of calcium.

The sparkling clearness of the natural waters of limestone regions is doubtless correlated with the solution of carbonate of lime, and the clearness of certain saline and alkaline waters has often been remarked. So-called "alkaline" waters in the Far West are often discolored, particularly with organic matter, but I have never seen them turbid with clay.*

Any considerable quantity of suspended carbonate of lime in water also affects the deposition of the clayey sediment, and calcareous delta deposits have special characters of their own. From what I can learn, some of the phenomena of the Nile delta, the material of which is described as a calcareous clay, are quite unlike those observed at the Mississippi delta, but my information is too meager to venture more than mere mention here.

The effect of sewage has also attracted attention. It has been claimed by a French writer that some river waters have been made clearer and better adapted to certain manufacturing uses by a slight sewage contamination. Numerous sanitary investigations have shown that waters contaminated by sewage to a very dangerous degree are often of exceptional pellucidity and sparkling clearness. In experiments on a clayey garden soil from the Connecticut Valley, which agitated with pure water retains the suspended matter with great tenacity, I found that minute quantities of sewage soon rendered it as clear as the very clearest natural waters, while the portion in pure water has a visible opalescence after six years' standing, the last three of which have been in a dark, quiet closet. "The Broad street pump," famous in sanitary literature, had great local popularity because of the sparkling clearness of its waters. Well-to-do people living miles away sent their servants with jugs for it, as a choice drinking water, because of this clearness, until it was closed by the authorities, after its sewage-contaminated waters had spread cholera into a multitude of homes, several hundred dying in a single month.

I think that where clay is precipitated by salts in the presence of organic matter which is partly in solution and partly in suspension (as sewage), the clay carries down with it much of the organic matter, probably in a sort of chemical combination similar to the "lake" formed by salts of alumina with dye-stuffs in dyeing.

* Since the reading of this paper it has been reported to me from several sources that even horses and mules in countries with alkaline waters soon learn that muddied waters are not alkaline, and choose muddy water for drinking

The water stored in reservoirs for the supply of cities sometimes in summer becomes offensive to the taste and smell, the cause being usually referred to the solution and decay of organic matter in the source of supply, or the growth and decay of low organisms in the reservoirs and distributing pipes. In New Haven, where I have carefully watched the phenomena in connection with the temperature and clearness of the water, on several occasions when such smell and taste was occurring heavy summer storms have roiled the waters, and each time this has taken place the special smell and taste have disappeared with the advent and precipitation of the suspended mud.

Water containing a very small proportion of organic albuminoid will putrefy and stink, and if this be mixed with sea-water or brackish water it becomes much more offensive to the smell than in fresh water, and there is an evolution of sulphureted hydrogen along with that of the putrid organic gases. I have experimented with dilute solutions of the albuminoids dissolved from marsh vegetation and from wood. If such dilute solution be mixed during the putrefactive stage with roiled water, a new set of phenomena occurs, and a considerable of the organic matter goes down with the clay as it subsides. I have not followed this up with satisfactory examinations of the precipitate, but some of the samples have strongly the odor of the offensive "blue mud" in the shallow harbors of our seaport towns. The sanitary bearings of this I alluded to in a paper a few years ago, but the facts have doubtless also their geological significance, and probably have something to do with the "mud-lump" phenomena at the mouth of the Mississippi. The occurrence of these "mud lumps" only in shoal salt or brackish water, and never in the fresh-water swamps, and the evolution of organic gases and of sulphureted hydrogen, are at least suggestive, and other phenomena relating to them are in accordance with some of the observations made in the experiments on the mutual reactions of decaying organic matter, brackish water, and suspended clay.

The effect of the common mineral acids on suspended clays is even more rapid than that of the salts. Some turbid waters are cleared more in five or ten minutes by the addition of sulphuric, nitric, or chlorohydric acids, or, better, mixtures of these, than in as many weeks or even months in pure water.

A considerable number of experiments have been made with acid similar to those described with salt by beginning with a stronger solution and reducing its strength when the material had settled, by decanting the clear portions, and adding an equal volume of distilled water. I may say here that the most of these experiments have been conducted in precipitating flasks made for the purpose, of hard glass, about a foot high, three inches in diameter at the base and one at the top. In some cases the whole of a portion of clay was treated; in others, after a watery suspension had stood several days, and when all the coarser particles had subsided, the upper part would be decanted, thoroughly mixed to insure uniformity, then divided into several portions for treatment in different ways for comparison with each other.

With those treated with acids the usual course has been to begin with clay in an acid or mixture of acids of known strength, amounting to 20 to 60 per cent. of the whole volume of the fluid under experiment, allowing it to settle, decant a given amount of the clear portion, and add the same amount of distilled water, the strength of the acid in the successive dilutions being calculated and the successive dilutions recorded.

With the mineral acids it has been the rule that at first the flocculation and precipitation are very rapid, the rapidity but slightly diminishing with great reductions of strength until the proportion of acid became very small; then there would be a marked increase in time needed, then finally and suddenly the subsiding would be as slow or slower than in pure water. One of the specimens exhibited to the Academy is of a fine clay from Hartford, Conn. I began with 60 per cent. nitro-

muriatic acid for, twelve successive dilutions and until the proportion of acid was by calculation almost infinitesimal (one part in several thousand of the liquid) one or two days was amply sufficient for clearing; the thirteenth cleared in nine days; the fourteenth in fourteen weeks; the fifteenth, after standing two and a half years, is still very obviously opalescent.

Two others are exhibited in which the behavior was similar, only the degree of dilution was not so great. One has stood thirty and the other thirty-two months, and the opalescence in each case is more marked than with companion portions which were begun in pure water only. In each case the precipitation was comparatively rapid until the proportion of acid amounted to less than one part in a thousand of the liquid, and in some the final long-continued suspension was only reached when the amount was very much less.

In some of the samples iridescent films or spicules have formed in the liquid, very like silica separated from solutions of dissolved glass; but the glass of the flasks used purported to be hard chemical glass, and I cannot test the samples without agitating them and thus bringing the experiments to a close. Similar glasses similarly treated have not become decomposed, and at present I think that the iridescent material is silica derived, not from the decomposition of the glass, but rather from a portion of the clay which may have undergone similar decomposition.

In the course of the experiments with acid solutions, as they reached a sufficient degree of dilution of acid and purity of water, there were the same picking up and suspension of material that was observed in the experiments with salt.

Caustic alkalies, potash, soda, and ammonia have also been used. Some authorities have stated that while acids and salts hasten sedimentation, alkalies check it and may even suspend it indefinitely. My experiments do not confirm this, but show rather the contrary effect. For example, the same Hartford clay which was used in experiments with salts and acids was used also with alkalies. A single illustration will suffice. Beginning with a solution containing one-half of 1 per cent. of pure caustic potash, the sedimentation was very much more rapid than in a similar portion in pure water, but not so rapid as samples with acids or salts. Operating on weaker and weaker solutions by successive decantations as before described, it would become nearly clear in twelve hours, when the proportion of potash in the solution was only .0008. When it was reduced to .0002 the behavior was then much as in pure water, and the sample is not yet entirely clear, after more than two years' standing.

So far as my experiments go, fine clays are precipitated from alkaline solutions more quickly and more completely than from pure water, no matter how dilute the solution.

When very fine soils, rich in organic matter (as, for example, some of the rich prairie bottom lands of Illinois), are agitated with water, there is much tendency, if the vessels are kept in the light, for a growth of confervoid algæ year after year, the decaying remains of which, diffused through the water, go down mostly with the clay, if agitated; but the solutions never become clear of the very light flocculent organic matter from the decaying algæ, now rising and now falling with changes of temperature and other conditions. Fresh agitation and settling may render it nearly clear for a time, but a new crop will spring up, its decayed remains to behave in the same way.

In experiments with neutral organic substances—crystalloids, like cane-sugar, and colloids, like extract of peat—there has been no law deduced; some hasten precipitation, others retard it, still others seem indifferent. I have experimented on the sugars along with yeast to observe the relations to fermentation, but this opens up a new set of reactions which I will not discuss here, the phenomena varying with the intensity of the action.

Early in the investigation I was led to believe that the behavior of the suspended particles of solids was different in the presence of crystalloid substances, as a class, from that in the presence of colloids, but at the present state of the investigation this is not proven.

The statements of some investigators lead to the inference that the rapidity of sedimentation is correlated with the activity of the "Brownian movements," and I have studied this part of the subject with especial interest.

The rapidity of the subsidence of the particles visible with the microscope appears to be related to this, and those substances which retard the "Brownian movements" hastens the precipitation. This applies to the fine grains of sand, flocculent clays, and such inert substances as pulverized charcoal. But I do not believe that the "Brownian movements" are continuously active in a liquid otherwise at rest, kept in a dark, quiet place, and where the changes of temperature are slight and take place very slowly. The conditions where these movements can be observed are necessarily those where various forms of radiant energy are manifest, and these are the probable active cause of the movements. It seems to me that where suspended clays are kept in the dark, and where there is little variation in temperature, we can hardly look to the energy of the "Brownian movements" as the active cause of the resistance to gravity and suspension of the heavier solid in the lighter liquid.

The later opalescence, which lingers so long, as well indeed as much of the more visible clay earlier, does not exist in the liquid as separately visible particles even with the microscope. All the microscopically visible particles settle relatively early in the experiment; the later opalescence is from ultramicroscopic materials. This is more visible in the sunlight than in ordinary diffused light, and shows the path of a beam of sunlight through it very strongly when the amount suspended is very slight indeed. The clearest natural waters, I have found, are not optically pure, but some appear to be without the opalescence that I have described from suspended clays.

Those portions of clay that remain long suspended, and are without separately visible particles, seem to me to be in a condition analogous to that of a colloid, reminding one of diluted gelatinous silica or diluted boiled starch. In many respects the behavior of that portion of a clay which will not settle to the bottom of a vessel a few inches deep in several days of quiet is that of a colloid. Prof. S. W. Johnson, whose knowledge of soils in their chemical and agricultural relations is so extensive, and who has been acquainted with these experiments during their progress, first suggested to me that the phenomena might be essentially chemical and to relate to the state of hydration of the clays.

Following this up, it seems to me probable that there may exist a series of hydrous silicates of alumina and iron, holding very feebly different amounts of water, and having different properties, so far as their relation to water is concerned, some swelling up in water more than others, and diffusible in it (as colloids) with different degrees of facility, and that acids, salts, heat, and other conditions change these states of hydration, and thus change the behavior of the suspended material towards water; that some which exist in pure water at one temperature are destroyed by another temperature, or by acids, salts, &c.

There are many indications that this is the case. The use of lime in agriculture for drying heavy, wet, clayey lands was known long before underdraining was extensively practiced. The burning of clays and other operations in agriculture may have their practical basis in the same chemical properties of clay. The tendency of many, and indeed most, clays when diffused in water to arrange themselves in layers or strata in the liquid suggests the same thing, these different strata representing different chemical compounds of a series. With some of the finer sedimentary clays it is not uncommon to have as many as six or eight such layers in the turbid liquid, and these probably represent different weak chemical compounds, settling with different degrees of rapidity, and more

or less colloid, or, if not soluble as a colloid, having different degrees of at
water. When some of these are slowly evaporated at low temperatures, the resu
bulky at first, colloidal in appearance, shrinking enormously on drying, and a
behaving very differently towards water. The effects of freezing and thawing are a

In short, there are many indications that clays (and perhaps other similar compo
certain conditions in water enter into new chemical combinations with the water, for
pounds having some colloidal characters, which compounds are stable only under a ver
range of conditions, but which are nevertheless of vast importance in the economy of natur
own experiments have extended to a relatively small number of substances, but chemical litera
of recent years mentions colloidal forms of various metallic oxides, and my experiments ma
illustrate but narrow phases of much wider-reaching phenomena.

Geological suggestions other than those already noted are sufficiently abundant, and have occurred all along the line of the investigation: suggestions pertaining to the segregation of veins, the phases of lamination in certain slates, the hardening of comminuted corals and shells into limestones, the effect of the alkaline salts evolved in the decomposition of rocks, the action and effects of alternately hot and cold waters on rocks and in veins—these and many other possible relations. The experiments were begun with very limited objects, but as they have gone on and widened with time they have suggested very many possibilities.